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GERMAN DEMOCRATIC REPUBLIC

PATENT

[seal] (12) Economic Patent

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(54) CHIP COVERING MATERIAL

(55) Chip covering material, epoxide-amine composite, aromatic diglycidyl
ethers (EPILOX), bisphenol-A diglycidyl ether, fillers, hardener amine, oligoether
amine, inks, temperature-resistant and climate-resistant materials.

(57) The invention concerns a process for the production of a chip covering
material based on epoxide-amine composites, which consist of a diepoxide or
polyepoxide, a filler, a hardener amine, an oligoether diamine, and ink. Chip covering
materials according to the invention are well-adhering materials on metal, glass, and
ceramic surfaces, and are resistant to temperature and climate.

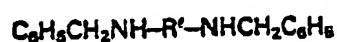
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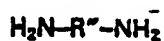
* May also indicate a "masking" or "resist" coating.--Trans. note

Pat nt Claims

1. Chip covering material of a specific processing characteristic based on aromatic diglycidyl ether and special hardener amines as well as powdered translucent fused quartz of a selected particle-size distribution and a soot addition of 0.1 wt. % is hereby characterized in that the amine component consists of a mixture of amines 1 and 2 in a molar ratio of 64:36 to 75:25, whereby amines 1 and 2 have the following significance:

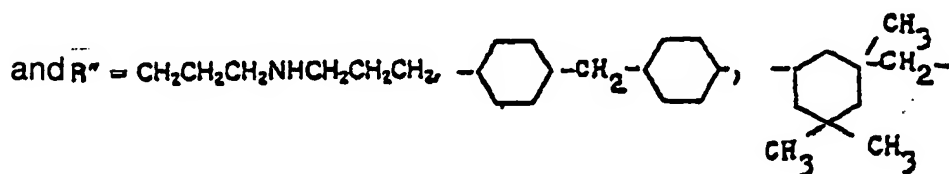


Amine 1



Amine 2

with $\text{R}' = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2, \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$



and the ratio of epoxide/NH functions amounts to 1:1, and a filler of 60-70 wt. % of a silanized powdered translucent fused quartz of a particle size smaller than 50 μm is produced, whereby 85-95 % of the particles lie between 2 and 50 μm , with an average particle size of 7-25 μm .

2. Chip covering material according to Claim 1, further characterized in that the system consists of two components A and B, which are intimately mixed prior to processing at 20-60°C and stirring under reduced pressure, whereby component A contains the epoxy resin, the soot component, and 65-75 % of the filler, and component B contains the amine mixture comprised of amines 1 and 2 and 25-35 % of the filler.

3. Chip covering material according to Claims 1 and 2, further characterized in that hardening is conducted thermally at 20-130°, but preferably stepwise at 40-80°C and 100-130°C.

Field of application of the invention

The invention concerns a chip covering material based on epoxide composites, which offers the special rheological processing properties and the climatic-mechanical and electrical-insulating properties required in branches of microelectronics.

Characteristics of the known technical solutions

Epoxy resin compounds have previously found a broad application as encapsulating agents for semiconductor devices, such as integrated circuits, transistors, diodes, and other electronic components. Usually such encapsulating means contain an epoxy resin, a hardener and accelerator, a coloring agent and a filler in a proportion that frequently amounts to more than 50 wt. %. Examples of encapsulating agents that contain amines or carboxylic acid anhydrides as hardeners are given in patents DE 3,137,898, DE 3,013,470 and US 4,042,550. The moisture sensitivity of the anhydride and the high hardening temperature ($T \geq 160^{\circ}\text{C}$), as well as the physiological/toxicological problems are problematical in the case of epoxide/anhydride systems. Covering materials, which contain aliphatic and/or cycloaliphatic amines, have an increased water absorption (Jahn, Epoxy Resins,

Publishers for the Base Materials Industry, Leipzig, 1969). In addition, the CO₂ absorption of the amines (DD 141,677)* also occurs in these systems, and this causes, apart from fluctuations in equivalence, in particular, an undesired foaming of the composite upon thermal hardening. This leads in turn to pores and cracks in the covering material, whereby there is no longer sufficient protection from climatic influences. The water absorption of epoxide-amine hardener systems has been very much reduced by the use of bulky aromatic amines (E. Morel, et al., Polymer 26 (1985) 1719). However, since these amines possess a considerably smaller reaction capacity than aliphatic amines and have poorer electrical insulation properties, their use is limited. Further, a solution is aimed at by reaction of aromatic, diprimary diamines with diglycidyl silane bonding agents, and this solution permits the production of a composite material with small water absorption and inner flexibility (DD-WP 207,105, DD-WP 204,098). Of course, the above-named disadvantages, which are caused by aromatic amines, are not eliminated. It has also been proposed to increase the fluctuating temperature load of covering materials by addition of components that make the material flexible, such as known reactive liquid polymers (butadiene/styrene/acrylonitrile copolymers) with a simultaneous reduction in water absorption (BF Goodrich, USA; Polym.-plast. Technol. Eng. 7 (1976) 27). The process of the invention, however, is not based on these solutions known from the patent and scientific literature.

* Number is somewhat illegible--possibly 141,877--Trans. note.

Objective of the invention

The objective of the invention consists of producing a chip covering material based on aromatic diglycidyl ethers (EPILOX), which is sufficient for the climatic-mechanical requirements of microelectronics and permits processing in existing technological procedures due to special rheological properties, and requires hardening temperatures that are lower ($T \leq 130^\circ\text{C}$) than epoxide-anhydride systems.

Representation of the essence of the invention

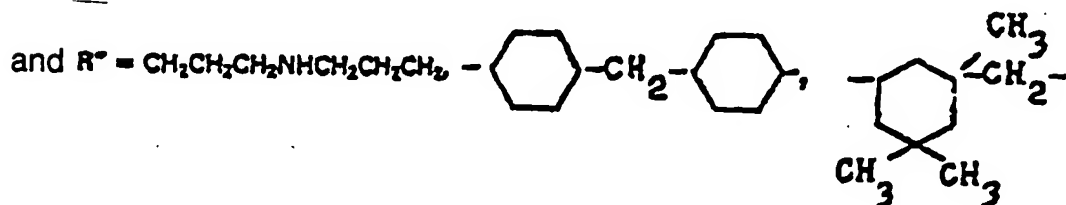
The task of the invention is to develop a chip covering material of a specific processing characteristic based on aromatic diglycidyl ether and special hardener amines, as well as powdered translucent fused quartz of a selected particle-size distribution and a soot addition of 0.1 wt. %. According to the invention, the task is resolved in that the amine component consists of a mixture of amines 1 and 2 in the molar ratio 64:36 to 75:25, whereby amines 1 and 2 have the following meaning and the ratio of NH/epoxide groups amounts to 1:1:



Amine 1



Amine 2



and 60-70 wt. % powdered translucent fused quartz of a particle size of less than 50 μm are utilized, whereby 85-95 % of the particles lie between 2 and 50 μm , with an average particle size of 7 to 25 μm .

Appropriately, the chip covering material consists of two separately storable components A and B, which are intimately mixed directly prior to processing into the ready-to-use chip covering material. Epoxide component A contains the epoxy resin, 65-75% of the filler, and 0.1 wt.% soot. The amine component B contains the amine mixture comprised of amines 1 and 2 and the rest of the filler (25 to 35%).

The separately weighed components are homogeneously mixed in vacuum with stirring and heating at 40°C to 60°C. A ready-to-use composite material is obtained after mixing equimolar quantities of the epoxide and the amine components. The chip covering material is then capable of casting for approximately 5 hours, flows completely into the chip contours and bonding wires and forms a stationary drop on the chip even in the unreacted state.

The thermal hardening required after coating the material onto the unprotected semiconductor chip is conducted at temperatures between 20 and 130°C, but preferably in several temperature steps at 40 to 80°C and 100 to 130 °C and requires 1 to 20 hours. The climatic-mechanical testing of chips, which have been protected with the chip covering materials of the invention, shows positive results in climatic-mechanical loading according to TGL 34789 (Table 1). An essential role for the functional capacity of the chip material is played by the high content of amine

component 1, since its internal flexibility assures a reduced CO₂ uptake and a relatively low hardening temperature. A composite material, which deviates from the composition according to the invention by reducing the fraction of amine 1 and, for example, contains amines 1 and 2 in the molar ratio 62:38, already displays clear defects and cannot be utilized as a chip covering material (comparative example 4, Table 1). The number of defects increases with a decreasing fraction of amine 1, so that a composite material with amines 1 and 2 in a molar ratio of 15:85 mol.%, as is provided for metal-metal adhesion in stomatologic practice (DD-WP 163,453), is unsuitable as a chip covering material.

If a filler other than that according to the invention is used, the climatic-mechanical tests can still be partially passed, but the rheological properties, which are necessary for processing in existing technological operating regimens can no longer be obtained. Either the composite material drips well from the metering device, but passes undesirably broadly onto the chip, or the material becomes intensely thixotropic, preventing a uniform coating from the metering device. It does not flow sufficiently and thus does not seal the semiconductor chip to be protected, including its bonding wires, in an error-free manner (free of bubbles).

Example 1

The production of the epoxide component (A) is conducted by homogeneously mixing in vacuum 9.000 g (26.44 mmoles) of bisphenol-A diglycidyl ether, 20.00 g of an

epoxy silane-coated powdered translucent fused quartz (particle size of 2-50 μm , average particle size of 10 μm) and 0.03 g of soot with slight heating and stirring.

The amine component (B) is produced from 1.126 g (6.61 mmoles) of 3-aminomethyl-3,5,5-trimethylcyclohexylamine, 4.344 g (13.23 mmoles) of N,N'-dibenzyl-3,6-dioxaoctanediamine-1,8, and 10.7 g of an epoxy silane-coated powdered translucent fused quartz (particle size of 2 to 50 μm) and stirred homogeneously in vacuum.

Components A and B are mixed homogeneously in vacuum in a weight ratio of 1.000:0.558 directly prior to use of the composite material. Then, this is coated onto the unprotected semiconductor chip, including the bonding wires. Thermal hardening is conducted for 2 hours at 60°C and for 16 hours at 120°C. The molar ratio of amines 1 and 2 amounts to 67:33.

Example 2

Analogously to Example 1, a chip covering material is prepared from :

A) epoxide component: 3.000 g (8.81 mmoles) of bisphenol-A diglycidyl ether, 6.000 g of an epoxy silane-coated powdered translucent fused quartz (particle size of 2-50 μm), 0.01 g of soot, and

B) amine component: 0.463 g (2.20 mmoles) of 4,4'-diaminodicyclohexylmethane, 1.450 g (4.41 mmoles) of N,N'-dibenzyl-3,6-

dioxaoctanediamine-1,8 and 4.440 g of an epoxy silane-coated powdered translucent fused quartz (particle size of 2 to 50 μm).

The ready-to-use chip covering material is obtained by mixing the epoxide and amine components in the weight ratio of 1.000:0.705. The molar ratio of amine 1 to hardener amine 2 amounts to 67:33. After coating of an approximately 1-cm wide stationary drop of the reacted composite material from a metering device, hardening is produced in two steps: 2 hours at 60°C and 16 hours at 120°C.

Example 3

A chip covering material is produced analogously to Example 1 from:

A) epoxide component: 12.000 g (35.25 mmoles) of bisphenol-A diglycidyl ether, 26.000 g of an epoxy silane-coated powdered translucent fused quartz (particle size of 2-50 μm) and 0.09 g of soot, and

B) amine component: 0.920 g (7.01 mmoles) of N,N-dipropylenetriamine, 6.000 g (17.62 mmoles) of N,N'-dibenzyl-5-oxanonanediamine-1,9 and 12.700 g of an epoxy silane-coated powdered translucent fused quartz (particle size of 2-50 μm).

The covering material that can be thermally hardened at 80°C/2 hours and 120°C/16 hours is produced by mixing the epoxide and amine components in the weight ratio of 1.000:0.515. The molar ratio of oligoether diamine to hardener amine amounts to 72:28.

Comparative Example 4

A composite material is produced from:

A) epoxide component: 9.000 g (26.44 mmoles) of bisphenol-A diglycidyl ether, 3 g of a dispersed silicic acid, and 0.02 g of soot, and

B) amine component: 1.358 g (6.47 mmoles) of 3-aminomethyl-3,5,5-trimethylcyclohexylamine, 3.473 g (10.58 mmoles) of N,N'-dibenzyl-3,6-dioxaoctanediamine-1,8, and 3.916 g of a dispersed silicic acid. The molar ratio of oligoether diamine to hardener amine amounts to 62:38. Hardening is produced as in Example 1. The climatic-mechanical test shows unacceptably high defects.

Table 1: Results of the climatic-mechanical test of encapsulating agents produced according to Examples 1 and 3, as well as Comparative Example 4; + no defects or a small number of defects. - defects, material unsuitable

	Patent examples		Comparative example
	1	3	4
1. Temperature fluctuation -40°C to 85°C	+	+	+
2. Moisture storage Db 40, 21 days	+	+	-
3. Temperature fluctuation of -55°C to 125°C	+	++	--

DEUTSCHE DEMOKRATISCHE REPUBLIK



(12) Wirtschaftspatent

Erteilt gemäß § 17 Absatz 1 Patentgesetz

PATENTSCHRIFT

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H 01 B 3/40

AMT FÜR ERFINDUNGS- UND PATENTWESEN

In der vom Anmelder eingereichten Fassung veröffentlicht

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(54) Chipabdeckmaterial

(55) Chipabdeckmaterial, Epoxid-Amin-Komposit, aromatische Diglycidylether (EPILOX), Bisphenol-A-diglycidylether, Füllstoff, Härteramin, Oligoetheramin, Einfärbemittel, temperaturbeständige und klimabeständige Materialien

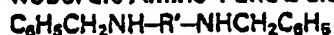
(57) Die Erfindung betrifft ein Verfahren zur Herstellung eines Chipabdeckmaterials auf der Basis von Epoxid-Amin-Kompositen, die bestehen aus einem Di- oder Polyepoxid, einem Füllstoff, einem Härteramin, einem Oligoetherdiamin und einem Einfärbemittel. Erfindungsgemäße Chipabdeckmaterialien sind temperatur- und klimabeständige, auf Metall-, Glas- und Keramikoberflächen gut haftende Materialien.

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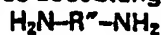
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Patentansprüche:

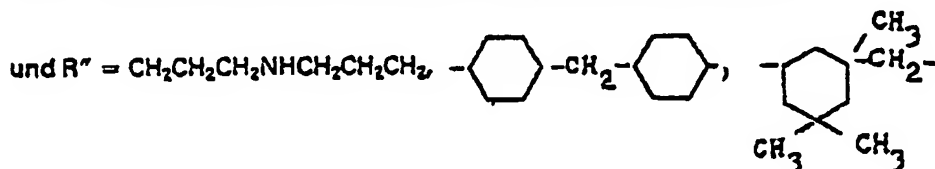
1. Chipabdeckmaterial einer bestimmten Verarbeitungscharakteristik auf Basis aromatischer Diglycidylether und spezieller Härteramine sowie Kieselgutmehl einer ausgewählten Korngrößenverteilung und einem Rußzusatz von 0,1 Ma.-%, dadurch gekennzeichnet, daß die Aminkomponente aus einer Mischung der Amine 1 und 2 im Molverhältnis 64:36 bis 75:25 besteht, wobei die Amine 1 und 2 die folgende Bedeutung haben:



Amin 1



Amin 2

mit $\text{R}' = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ 

und das Verhältnis von Epoxid/NH-Funktion 1:1 beträgt, und eine Füllung mit 60 bis 70 Ma.-% eines silanisierten Kieselgutmehls einer Korngröße kleiner 50 µm erfolgt, wobei 85–95 % zwischen 2 und 50 µm liegen, mit einer durchschnittlichen Korngröße von 7 bis 25 µm.

2. Chipabdeckmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das System aus zwei Komponenten A und B besteht, die vor der Verarbeitung bei 20 bis 60°C und Rühren unter vermindertem Druck innig vermischt werden, wobei die Komponente A das Epoxidharz, den Rußanteil und 65 bis 75 % des Füllstoffes enthält und die Komponente B das Amingemisch aus Amin 1 und 2 und 25 bis 35 % des Füllstoffes enthält.
3. Chipabdeckmaterial nach Anspruch 1 und 2, dadurch gekennzeichnet, daß die Härtung thermisch bei 20 bis 130°C erfolgt, vorzugsweise jedoch stufenweise bei 40 bis 80°C und 100 bis 130°C.

Anwendungsgebiet der Erfindung

Die Erfindung betrifft ein Chipabdeckmaterial auf Basis von Epoxid-Kompositen, das den speziellen rheologischen Verarbeitungseigenschaften und den klimatisch-mechanischen und Elektroisoler-Eigenschaftsanforderungen der Mikroelektronikbranche entspricht.

Charakteristik der bekannten technischen Lösungen

Epoxidharzmassen fanden bisher eine breite Anwendung als Einkapselungsmittel für Halbleitereinrichtungen, wie integrierte Schaltkreise, Transistoren, Dioden und andere elektronische Bauteile. Gewöhnlich enthalten derartige Einkapselungsmittel ein Epoxidharz, einen Härter und Beschleuniger, ein Färbemittel und einen Füllstoff in einem Anteil, der häufig über 50 Gew.-% beträgt. Beispiele für Einkapselungsmittel, die Amine oder Carbonsäureanhydride als Härter enthalten, sind in den Patentschriften DE 3137 898, DE 3013 470, US 4042 550 gegeben. Problematisch ist bei Epoxid/Anhydrid-Systemen die Feuchtigkeitsempfindlichkeit des Anhydrids und die hohen Aushärtetemperaturen ($T \geq 160^\circ\text{C}$) sowie ihre physiologisch/toxikologische Belastung. Abdeckmaterialien, die aliphatische oder/und cycloaliphatische Amine enthalten, weisen eine erhöhte Wasseraufnahme auf (Jahn, Epoxidharze, Verlag für Grundstoffindustrie, Leipzig 1969). Hinzu kommt bei diesen Systemen noch die CO_2 -Aufnahme der Amine (DD 141 877), die abgesehen von Äquivalenzabweichungen vor allem ein unerwünschtes Aufschäumen des Komposits bei der thermischen Härtung verursacht. Das führt wiederum zu Poren und Rissen im Abdeckmaterial, womit ein ausreichender Schutz vor klimatischen Einflüssen nicht mehr gegeben ist. Die Wasseraufnahme von Epoxid-Amin-Härtersystemen wurde durch sperrige aromatische Amine stark erniedrigt (E. Morel et al., Polymer 28 (1985) 1719). Da diese Amine jedoch eine erheblich geringere Reaktionsfähigkeit als aliphatische Amine besitzen und schlechtere Elektroisolationseigenschaften aufweisen, ist ihre Verwendung eingeschränkt. Ferner ist durch Umsetzung von aromatischen diprimären Diaminen mit Glycidylsilan-Heftvermittlern eine Lösung angestrebt worden, die die Herstellung eines Kompositmaterials mit geringer Wasseraufnahme und innerer Flexibilisierung gestattet (DO-WP 207 105, DO-WP 204098). Allerdings werden die oben genannten Nachteile, die durch aromatische Amine verursacht werden, nicht beseitigt. Es ist auch vorgeschlagen worden, die Temperaturwechselbelastung von Abdeckmaterialien durch Zusatz flexibilisierend wirkender Komponenten wie der bekannten reaktiven Flüssigpolymere (Butadien/Styren/Acrylnitril-Copolymere) zu erhöhen bei gleichzeitiger Absenkung der Wasseraufnahme (Firmenschrift BF Goodrich, USA; Polym.-plast. Technol. Eng. 7 (1976) 27). Diese aus der Patent- und wissenschaftlichen Literatur bekannten Lösungen berühren jedoch nicht das erfindungsgemäße Verfahren.

Ziel der Erfindung

Das Ziel der Erfindung besteht in der Herstellung eines Chipabdeckmaterials auf Basis von aromatischen Diglycidylethern (EPILOX), das den klimatisch-mechanischen Anforderungen der Mikroelektronik genügt und durch spezielle rheologische Eigenschaften eine Verarbeitung im vorhandenen technologischen Regime erlaubt und niedrigere Aushärtetemperaturen ($T \leq 130^\circ\text{C}$) erfordert als Epoxid-Anhydrid-Systeme.

Beispiel 3

Analog Beispiel 1 wird ein Chipabdeckmaterial hergestellt aus

A) Epoxidkomponente: 12,000 g (35,25 mmol) Bisphenol-A-diglycidylether, 26,000 g eines epoxysilanbeschichteten Kieselgutmehls (Korngröße 2 bis 50 µm) und 0,08 g Ruß und

B) Aminkomponente: 0,920 g (7,01 mmol) N,N-Dipropylentriamin, 8,000 g (17,82 mmol) N,N'-Dibenzyl-5-oxanonandiamin-1,9 und 12,700 g eines epoxysilanbeschichteten Kieselgutmehls (Korngröße 2 bis 50 µm).

Das thermisch bei 80°C/2 Stunden und 120°C/18 Stunden aushärtbare Abdeckmaterial wird durch Vermischen von Epoxid- und Aminkomponente im Masseverhältnis 1,000:0,515 hergestellt. Das Molverhältnis Oligoetherdiamin zu Härteramin beträgt 72:28.

Vergleichsbeispiel 4

Es wird ein Kompositmaterial hergestellt aus

A) Epoxidkomponente: 9,000 g (26,44 mmol) Bisphenol-A-diglycidylether, 3 g einer dispersen Kieselsäure und 0,02 g Ruß und
B) Aminkomponente: 1,358 g (6,47 mmol) 3-Amino-methyl-3,5,5-trimethylcyclohexylamin, 3,473 g (10,58 mmol) N,N'-Dibenzyl-3,6-dioxaoctandiamin-1,8 und 3,918 g einer dispersen Kieselsäure. Das Molverhältnis von Oligoetherdiamin zur Härteramin beträgt 62:38. Die Härtung erfolgt wie bei Beispiel 1. Die klimatisch-mechanische Prüfung zeigt unakzeptabel hohe Ausfälle.

Tabelle 1: Ergebnisse der klimatisch-mechanischen Testung von nach Beispiel 1 und 3 hergestellten Einkapselungsmitteln, sowie Vergleichsmuster 4; + keine oder geringe Anzahl an Ausfällen, - Ausfälle, Material ungeeignet.

	Patentbeispiele		Vergleichsmuster
	1	3	4
1. Temperaturwechsel -40°C bis 85°C	+	+	+
2. Feuchtelagerung Ob 40, 21 Tage	+	+	-
3. Temperaturwechsel -65°C bis 125°C	+	++	---